ndian J. Phys. 77B (5), 519-523 (2003)

AN INTERNATIONAL JOURNAL
IJP

Molecular interaction study in binary mixtures of N, N-dimethylacetamide with 2-ethoxyethanol at three different temperatures

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Received 3 March 2003, accepted 28 July 2003

Abstract Densities, viscosities and ultrasonic velocities of the binary mixture of 2-ethoxyethanol (EE) with different mole fractions of N,N-dimethylacetamide (DMA) have been measured at 298.15, 308.15 and 318.15K. From the experimental data, isentropic compressibility, intermolecular free length, acoustic impedance, molar sound speed and some of their respective excess properties were calculated. The computed results have been fitted to the Redlich-Kister polynomial to estimate the binary coefficients and standard deviations. Deviation of excess properties have been explained in terms of the interaction between unlike molecules in the binary mixtures.

Keywords Density, viscosity, ultrasonic velocity, excess properties, binary mixtures

PACS Nos. 43.35.Bf, 06.30.Dr, 66.20.+d

1. Introduction

Thermodynamic excess properties of the binary liquid mixtures have been very useful to obtain information on the intermolecular interactions and geometrical effects in the systems [1, 2]. Solvents like 2-ethoxyethanol (EE) commercially known as 'cellosolves', are widely used as components of solvents, co-emulsifiers and stabilisers of emulsions, dyes and lacquers [3]. They can be considered to be ethylene glycol derivatives obtained by the replacement of one of the hydroxy groups by an alkoxy group. Their molecules contain both hydroxylic and ether groups (as well as an alkyl group). The cellosolves in their pure state, are self-associated and form cyclic dimers in which the hydroxy proton of one cellosolve molecule is bound to the ether oxygen atom of the other [4-7]. They can also form intramolecularly hydrogen bonded five membered ring monomers [4,5,8-10]. In view of their properties and structure the 2-ethoxyethanol is often regarded as 'quasi-aprotic' solvent [11]. On the other hand N,N-dimethylacetamide (DMA) is a dipolar aprotic solvent and due to the moderate dielectric constant (ε = 37.8 at 298.15K) [12], it is likely to be moderately structured. In this paper, we made an attempt to study the behaviour of a dipolar aprotic solvent in a binary mixture with a 'quasi-aprotic' solvent over the entire range of their compositions at 298.15, 308.15 and 318.15K by measurement of their densities, viscosities and ultrasonic velocities. From these experimental data excess volume (v^E), excess viscosity ($\Delta\eta$), excess intermolecular free length (L_f^E) and isentropic compressibility changes (β^E) were calculated. The close relationship of N,N-dimethylacetamide to peptide linkage[13] also has another important dimension to the present investigation.

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2. Experimental

N,N-dimethylacetamide (SRL, India) was shaken well with charged CaO (AR, BDH) for 1-2 hours, kept overnight, decanted and distilled twice. The middle fraction was collected and used. Its density (936.4 Kg m^{-3}) and viscosity (0.9329×10^{-3} Kg m^{-1} s^{-1}) at 298.15K compared well with the literature values [12]. 2-ethoxyethanol (Merck, India) was kept overnight with anhydrous K_2CO_3, decanted and distilled in an all glass distillation set and the middle fraction was collected. The purified solvent had a density 925.0 Kg m^{-3} [14] and a viscosity 1.8243×10^{-3} Kg m^{-1} s^{-1} at 298.15 K.

Densities were measured with an Ostwald-Sprengel type pycnometer having a bulb volume of about 25 cm^3 and an internal diameter of the capillary of about 1 mm. The pycnometer was calibrated at (298.15, 308.15 and 318.15)K with triply distilled water and benzene. The reproducibility of the density measurement was $\pm 3 \times 10^{-5}$ g cm^{-3}. The temperature of the thermostatic bath was controlled to ± 0.01K of the desired temperature.

The kinematic viscosities were measured by means of a suspended – level Ubbelohde viscometer with a flow time of about 539s for distilled water at 298.15K. The time of efflux was measured with a stop watch capable of recording ± 0.1s. The viscometer containing the test liquids was always kept in a vertical position and was allowed to stand for about 30 minutes in a thermostatic water bath controlled to ± 0.01K so that the thermal fluctuation in the viscometer was minimized. The estimated error of the viscosity measurements was ± 0.2%. Sound velocities were measured, with an uncertainty of ± 0.3%, using a single-crystal variable-path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at 4MHz, which was calibrated with water, methanol and benzene at each temperature. The temperature stability was maintained within ± 0.01K by circulating thermostated water around the cell with a circulating pump.

In all cases, the experiments were performed at least in five replicates for each composition and at each temperature, and the results were averaged.

3. Results and discussion

The experimental values of density ρ, viscosity η, and ultrasonic velocity u, of pure liquids and their binary mixtures at three different temperatures, have been used to calculate the values of isentropic

Table 1. Values of experimental density (ρ), absolute viscosity(η), ultrasonic velocity (u), isentropic compressibility (β), intermolecular free length (L_f), relative association (R_A), acoustic impedance (Z) and molar sound speed (R_m) of binary mixtures of DMA and EE at 298.15, 308.15 and 318.15K

x_1 (DMA)	ρ (kg m^{-3})	η (10^{-3}kg $m^{-1}s^{-1}$)	u (ms^{-1})	β ($10^{-10}m^2N^{-1}$)	L_f (10^{-11}m)	R_A	Z (10^6kg $m^{-2}s^{-1}$)	R_m [$10^4m^3mol^{-1}(ms^{-1})^{1/3}$]
				T = 298.15K				
0.000	925.0	1.8243	1306.9	6.3290	5.1746	1.0000	1.2089	10.6518
0.0500	926.0	1.8031	1316.6	6.2300	5.1337	0.9986	1.2192	10.6489
0.1042	926.9	1.7780	1327.3	6.1235	5.0899	0.9969	1.2303	10.6480
0.1500	927.6	1.7517	1335.7	6.0420	5.0560	0.9955	1.2390	10.6461
0.2075	928.6	1.7147	1345.5	5.9485	5.0164	0.9942	1.2494	10.6400
0.2500	929.2	1.6834	1352.7	5.8808	4.9881	0.9931	1.2569	10.6369
0.3097	930.0	1.6350	1362.6	5.7910	4.9497	0.9915	1.2672	10.6323
0.3650	930.8	1.5868	1371.5	5.7113	4.9155	0.9902	1.2766	10.6264
0.4111	931.4	1.5449	1378.8	5.6480	4.8879	0.9891	1.2842	10.6219
0.4600	931.9	1.4986	1386.4	5.5824	4.8598	0.9878	1.2919	10.6181
0.5115	932.6	1.4473	1394.4	5.5151	4.8301	0.9866	1.3004	10.6119
0.5650	933.1	1.3916	1402.6	5.4474	4.8006	0.9853	1.3087	10.6078
0.6110	933.6	1.3433	1409.5	5.3910	4.7758	0.9842	1.3159	10.6029
0.6550	934.0	1.2968	1416.1	5.3385	4.7525	0.9831	1.3226	10.5990
0.7096	934.5	1.2391	1424.0	5.2770	4.7249	0.9818	1.3307	10.5933
0.7550	934.9	1.1912	1430.4	5.2282	4.7027	0.9807	1.3373	10.5881
0.8073	935.2	1.1359	1437.3	5.1756	4.6794	0.9795	1.3441	10.5828
0.8500	935.5	1.0907	1443.1	5.1326	4.6599	0.9785	1.3500	10.5782
0.9041	935.9	1.0339	1450.3	5.0795	4.6357	0.9773	1.3573	10.5716
1.000	936.4	0.9329	1463.5	4.9860	4.5927	0.9748	1.3704	10.5630
				T = 308.15K				
0.0000	916.4	1.4800	1274.4	6.7180	5.4304	1.0000	1.1678	10.6619
0.0500	917.4	1.4668	1284.5	6.6067	5.3830	0.9985	1.1784	10.6606
0.1042	918.4	1.4522	1295.3	6.4895	5.3352	0.9967	1.1896	10.6594
0.1500	919.1	1.4369	1303.8	6.4006	5.2984	0.9953	1.1983	10.6583
0.2075	920.1	1.4129	1313.5	6.2994	5.2565	0.9939	1.2085	10.6525
0.2500	920.7	1.3916	1320.5	6.2291	5.2269	0.9929	1.2158	10.6493
0.3097	921.5	1.3573	1329.9	6.1357	5.1877	0.9914	1.2255	10.6438
0.3650	922.3	1.3224	1338.3	6.0536	5.1529	0.9901	1.2343	10.6371
0.4111	922.9	1.2913	1345.2	5.9880	5.1248	0.9894	1.2415	10.6319
0.4600	923.5	1.2566	1352.4	5.9206	5.0958	0.9880	1.2489	10.6263
0.5115	924.1	1.2174	1359.8	5.8520	5.0665	0.9868	1.2566	10.6203
0.5650	924.7	1.1747	1367.4	5.7834	5.0367	0.9856	1.2644	10.6138
0.6110	925.2	1.1375	1373.9	5.7260	5.0115	0.9846	1.2711	10.6083
0.6550	925.6	1.1017	1380.1	5.6721	4.9879	0.9835	1.2774	10.6038
0.7096	926.1	1.0570	1387.6	5.6081	4.9596	0.9823	1.2850	10.5975
0.7550	926.5	1.0197	1393.7	5.5567	4.9368	0.9813	1.2913	10.5919
0.8073	926.9	0.9773	1400.6	5.4998	4.9115	0.9801	1.2982	10.5859
0.8500	927.2	0.9422	1406.3	5.4539	4.8908	0.9791	1.3039	10.5813
0.9041	927.5	0.8981	1413.5	5.3961	4.8650	0.9778	1.3110	10.5763
1.0000	927.9	0.8204	1426.3	5.2970	4.8204	0.9752	1.3234	10.5686

(Contd

Table 1. *(Contd.)*

				T = 318.15K				
0.000	907.9	1.2220	1242.2	7.1380	5.6956	1.000	1.1278	10.6714
0.0500	908.8	1.2135	1252.5	7.0134	5.6459	0.9982	1.1383	10.6708
0.1042	909.8	1.2060	1263.5	6.8850	5.5937	0.9964	1.1495	10.6706
0.1500	910.6	1.1986	1271.9	6.7878	5.5543	0.9951	1.1582	10.6693
0.2075	911.5	1.1840	1281.2	6.6780	5.5113	0.9937	1.1678	10.6641
0.2500	912.1	1.1697	1288.4	6.6043	5.4787	0.9925	1.1751	10.6618
0.3097	912.9	1.1456	1297.5	6.5067	5.4379	0.9910	1.1845	10.6561
0.3650	913.7	1.1204	1305.6	6.4210	5.4018	0.9898	1.1929	10.6490
0.4111	914.2	1.0974	1312.2	6.3524	5.3731	0.9887	1.1990	10.6456
0.4600	914.8	1.0708	1319.0	6.2823	5.3437	0.9876	1.2066	10.6383
0.5115	915.4	1.0402	1326.1	6.2120	5.3133	0.9865	1.2139	10.6319
0.5650	916.0	1.0070	1333.2	6.1413	5.2833	0.9854	1.2212	10.6246
0.6110	916.5	0.9779	1339.3	6.0823	5.2578	0.9844	1.2274	10.6183
0.6550	916.9	0.9499	1345.2	6.0263	5.2336	0.9834	1.2334	10.6134
0.7096	917.4	0.9146	1352.5	5.9589	5.2039	0.9822	1.2408	10.6070
0.7550	917.8	0.8850	1358.5	5.9041	5.1798	0.9812	1.2468	10.6016
0.8073	918.2	0.8519	1365.4	5.8420	5.1525	0.9799	1.2537	10.5959
0.8500	918.4	0.8242	1371.0	5.7927	5.1309	0.9788	1.2591	10.5926
0.9041	918.7	0.7893	1378.4	5.7292	5.1025	0.9774	1.2663	10.5885
1.0000	919.1	0.7285	1390.9	5.6230	5.0556	0.9749	1.2783	10.5808

Table 2. Coefficients A_i of eq (8) and standard deviations $\sigma(Y^E)$ for binary mixtures N,N-dimethylacetamide +2-ethoxy ethanol at 298.15, 308.15 and 318.15K

Function	A_1	A_2	A_3	A_4	A_5	$\sigma(Y^E)$
			T = 298.15K			
V^E (10^6m^{3}mol^{-1})	-0.0014	-0.8416	1.0933	-0.4183	0.1686	0.0005
$\Delta\eta$ (10^3N m^{-2}S)	-0.0013	0.5766	-1.1516	0.7099	-0.1330	0.0001
$\Delta\beta$ (10^{10}m^{2}N^{-1})	-0.0045	-0.8271	2.8121	-4.0417	2.0783	0.0126
L_f^E (10^{11}m)	-0.0004	-0.2618	0.4654	-0.3143	0.1121	0.0001
			T = 308.15K			
V^E (10^6m^{3}mol^{-1})	-0.0010	-0.9418	1.4826	-1.0197	0.4817	0.0004
$\Delta\eta$ (10^3N m^{-2}S)	-0.0021	0.5257	-0.9811	0.5069	-0.0484	0.0002
$\Delta\beta$ (10^{10}m^{2}N^{-1})	-0.0003	-0.9347	1.9575	-1.5724	0.5515	0.0003
L_f^E (10^{11}m)	-0.0007	-0.3639	0.8033	-0.6913	0.2534	0.0001
			T = 318.15K			
V^E (10^6m^{3}mol^{-1})	-0.0008	-1.0313	1.8262	-1.5570	0.7655	0.0004
$\Delta\eta$ (10^3N m^{-2}S)	-0.0029	0.4746	-0.8098	0.3019	0.0374	0.0003
$\Delta\beta$ (10^{10}m^{2}N^{-1})	-0.0014	-1.2952	3.3347	-3.3269	1.2921	0.0019
L_f^E (10^{11}m)	0.0001	-0.4213	0.9674	-0.8389	0.2929	0.0001

compressibility β, intermolecular free length L_f, relative association R_A, acoustic impedance Z and molar sound speed R_m using the following standard relations :

$$\beta = 1/u^2\rho, \tag{1}$$

$$L_f = K/u\rho^{1/2}, \tag{2}$$

$$R_A = (\rho/\rho_0)(u_0/u)^{1/3}, \tag{3}$$

$$Z = u\rho, \tag{4}$$

$$R_m = Vu^{1/3}, \tag{5}$$

where K is a temperature-dependent constant [= (93.875 + 0.375 T) x 10^{-8} [15], T is the absolute temperature; ρ_0, ρ and u_0, u are the densities and ultrasonic speeds of the solvent (2-ethoxyethanol) and solution, respectively. The molar volume (V) of the binary mixtures was calculated using the equation

$$V = \frac{M_1X_1 + M_2X_2}{} \tag{6}$$

where M_1 and M_2 are the molecular masses of pure substances and ρ is the density of the mixture. The values of $\rho, \eta, u, \beta, L_f$, R_A, Z and R_m as a function of mole fraction X_1 of DMA at 298.15, 308.15 and 318.15K are listed in Table 1. The nonlinear increase/decrease in $\rho, \eta, u, \beta, L_f$, R_A, Z and R_m values (Table 1) with composition indicates significant interactions between the component molecules.

The excess functions are found to be more sensitive towards intermolecular interactions in liquid mixtures. The excess volume V^E, excess intermolecular free length L_f^E, viscosity deviations $\Delta\eta$ and excess isentropic compressibility β^E have been calculated using the following relation :

$$Y^E = Y - [x_1Y_1 + x_2Y_2], \tag{7}$$

where Y^E is V^E or L_f^E or $\Delta\eta$ or β^E ; x is mole fraction of pure solvent in

the mixture and subscripts 1 and 2 stand for DMA and 2-ethoxyethanol respectively.

Graphical representations of V^E, L_f^E, $\Delta\eta$ and $\Delta\beta$ as function of mole fraction of *N,N*-dimethylacetamide are given in Figures 1-4, respectively.

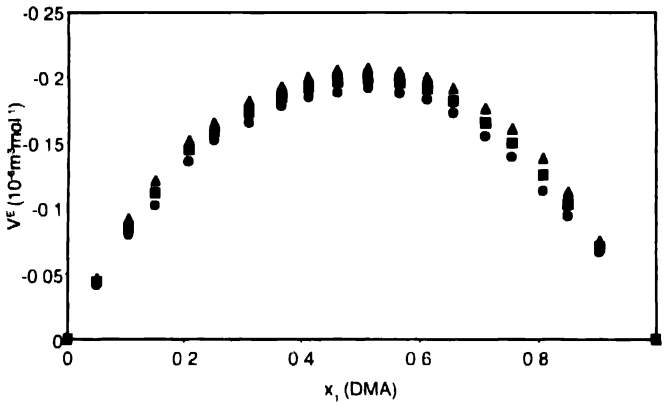

Figure 1. Variation of excess volume (V^E) *versus* mole fraction (x_1) of DMA at 298 15K (•) , 308 15K (■) , 318.15 K(▲)

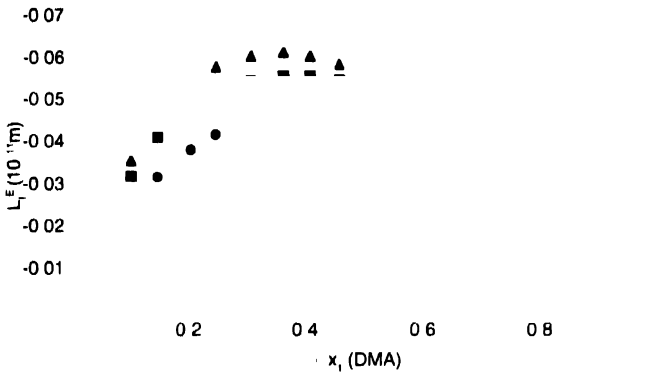

Figure 2. Variation of intermolecular free length (L_f^E) *versus* mole fraction (x_1) of DMA at 298 15K (•) ; 308 15K (■) , 318 15K (▲)

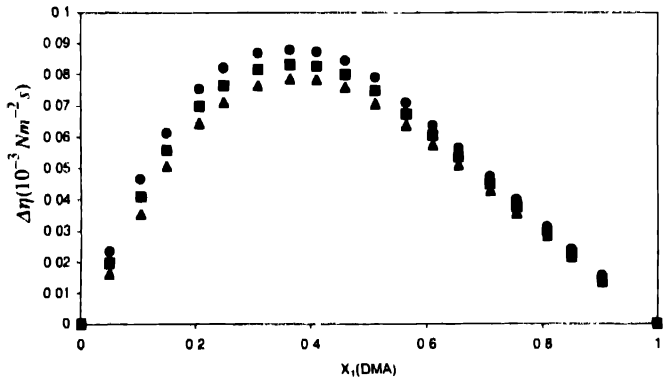

Figure 3. Variation of excess viscosity ($\Delta\eta$) *versus* mole fraction (x_1) of DMA at 298 15K (•) , 308.15K (■) , 318.15K (▲)

The excess properties Y^E were fitted to the Redlich – Kister equation [15]

$$Y^E = x_1(1-x_1)\sum A_j(1-2x_1)^j, \qquad (8)$$

where A_0, A_1, A_2 are adjustable parameters. These parameters were evaluated by fitting $Y^E / x_1(1-x_1)$ to eq. (8) by the method of least squares. The values of these parameters along with standard deviation $\sigma(Y^E)$ of Y^E as defined by the equation

$$\sigma(Y^E) = \left[\sum\left(Y^E_{obs} - Y^E_{calc}\right)^2 / (N-M)\right]^{0.5}, \qquad (9)$$

are recorded in Table 2. In eq. (9), N is the total number of experimental points and M is the number of parameters.

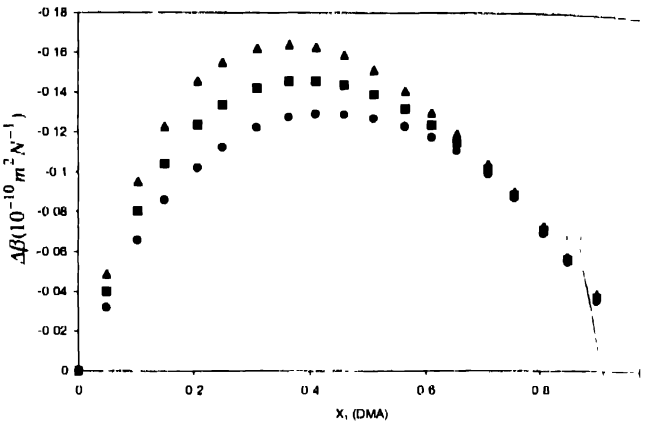

Figure 4. Variation of excess isentropic compressibility ($\Delta\beta$) versus mole fraction (x_1) of DMA at 298.15K (•) ; 308 15K (■), 318 15K (▲)

It is observed from Table 1 that u and Z increase while β, L_f, R_A and R_m decreases as mole fraction (x_1) of DMA increases in the mixture The decrease in β and L_f with x_1 in the present investigation, indicates significant interaction between DMA and EE molecules. The addition of DMA to alkoxy alkanol tends to cause breaking of self-associated alkanol molecules with a consequent increase in u and L_f. However, because of simultaneous formation of strong hydrogen bonds between the unlike molecules, there is a compensating effect resulting in an overall decrease in β and L_f or increase in u with x_1. The rise in temperature makes the intermolecular free length to increase as expected due to the thermal expansion of the liquid medium In the present investigation, relative association R_A is found to decrease with mole fraction of DMA at all the three temperatures The result signifies that unlike interactions are relatively weak compared to like interactions in the studied mixture. A slight increase in Z with x_1 also supports weak interaction between DMA and EE molecules.

The system *N,N*-dimethylacetamide + 2-ethoxyethanol shows negative V^E and L_f^E values over the entire range of mole fraction and over the range of temperatures studied as given in Figures 1 and 2. The system shows broad minima of V^E and L_f^E at a mole fraction of about 0.5 and 0.4 of DMA respectively. The observed V^E and L_f^E values may be explained from several effects which can be divided into physical, chemical and geometrical contributions. The physical interactions involve mainly dispersion forces giving a positive contribution

to V^a and L_f^E. The chemical or specific interactions result due to forming and/or breaking of hydrogen bonds and other complex-forming interactions. It is well known that alkoxy ethanols exist as associated structures like the alcohols [11, 16] in the liquid state; the association may be due to the intramolecular hydrogen bond formation between the ether oxygen atom and the – OH group. The interaction between a moderately structured DMA and 2-ethoxyethanol may disrupt the hydrogen bonds in 2-ethoxyethanol molecules, accompanied by weak hydrogen bond formation between the unlike molecules and thus offer a negative contribution to V^E [17] and L_f^E.

The *N,N*-dimethylacetamide + 2-ethoxyethanol system displays a sharp positive deviation of $\Delta\eta$ over the entire mole fraction range and over the three temperatures investigated (Figure 3). The positive deviation from a rectilinear dependence on mole fraction of DMA indicates the predominance of hydrogen bonding interactions between the unlike molecules (DMA and EE) over the dissociation effects in the system. With the rise in temperature, the $\Delta\eta$ values become less and less positive indicating a tendency of the decrease of these interactions thereby the system approaches ideal behaviour. The results of deviations in isentropic compressibility *versus* mole fraction of DMA has been represented in Figure 4. The figure shows that the values of $\Delta\beta$ are negative over the entire composition range and at all the three studied temperatures, suggesting a predominant hydrogen bond interaction between DMA and 2-ethoxyethanol and thereby causing an increase in the ultrasonic velocity and a decrease in the compressibility of this solution. The process continues until the minima is reached and then these parameters follow the reverse trend.

Thus from the present investigation, it may be concluded that due to the presence of highly polar ether group in 2-ethoxyethanol molecule, the hydrogen bonding interaction is playing a predominant role over dispersion and other forces that are likely to be operative in non-aqueous solvent mixtures. This interaction accompanied by a minor disruption of 2-ethoxyethanol structure is responsible for the negative contribution of excess values in the experimental data.

Acknowledgment

Financial assistance by the University Grants Commission extended through Departmental Research Support (DRS) Project in Chemistry is acknowledged.

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